# Addition of Halogenocarbons or Dihydrogen to Alkenes in the Presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$: Catalysis by a Dinuclear Species

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Addition of halogenocarbons or dihydrogen to alkenes in the presence of $[Fe_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (**1**) has been shown to proceed by a non-radical catalytic cycle in which a dinuclear species, probably $[Fe_2(CO)_3(\eta\text{-}C_5H_5)_2]$, is the active catalyst.

We have previously studied the mechanism of the addition of halogenocarbons to alkenes (equation 1) in the presence of $[Mo_2(CO)_6(\eta\text{-cp})_2]$ (cp = $C_5H_5$),[1] $[RuCl_2(PPh_3)_3]$,[2] and $[Cr(CO)_3(\eta^6\text{-}C_{10}H_8)]$[3] and have shown that, in all cases, the reactions are catalysed by a metal species, but that free radical intermediates are involved. We now report a study of this reaction in the presence of $[Fe_2(CO)_4(\eta\text{-cp})_2]$ (**1**). This complex has previously been shown to be capable of promoting reaction (1).[4]

$$RCH{=}CH_2 + CX_4 \rightarrow RCHXCH_2CX_3 \qquad (1)$$

Reactions between $CCl_4$ and oct-1-ene were performed at 40, 80, 100, and 120 °C and yields of the 1:1 adduct,

**Table 1.** Yield of 1 : 1 adduct from reaction of oct-1-ene and $CCl_4$.[a]

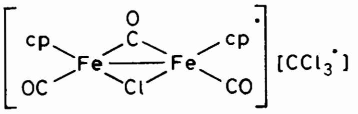
| Catalyst | Temp./°C | Yield (%)[b] |
|---|---|---|
| $[Fe_2(CO)_4(\eta\text{-}cp)_2]$ **(1)** | 40 | 7.4 |
| | 80 | 32.0 |
| | 100 | 50.0 |
| | 120 | 62.0 |
| $[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(3)** | 40 | 6.3 |
| | 100 | 60.0 |
| | 120 | 72.0 |

[a] Reactions were between oct-1-ene (1.5 g) and $CCl_4$ (8.0 g) in the presence of the appropriate catalyst ($1.4 \times 10^{-4}$ mol) in sealed tubes in the dark for 15 h. [b] Yields based upon amounts of alkene charged, rather than consumed.

$[M_2(CO)_4(\eta\text{-}cp)_2]$

**(1)** M = Fe

**(7)** M = Ru



**(2)**

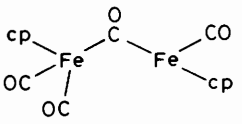
$[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$

**(3)**

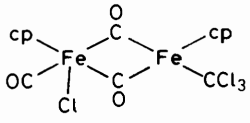
$[Fe_2(CO)_3(\eta\text{-}C_5R_5)_2]$

**(4)** R = H

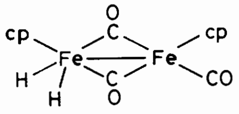
**(5)** R = Me



**(6)**



**(8)**

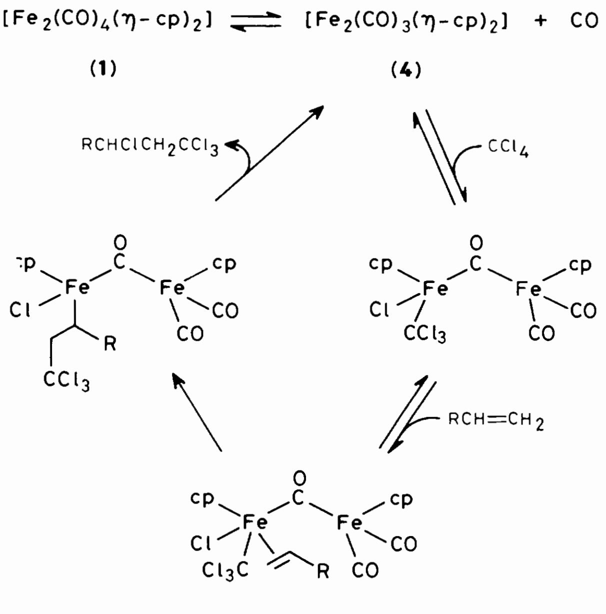


**(9)**

1,1,1,3-tetrachlorononane, are shown in Table 1. These indicate that complex **(1)** is capable of promoting the reaction, even at the lower temperatures, and is playing the role of either a catalyst or a radical chain initiator. Reaction in the presence of **(1)** proceeds with approximately equal efficiencies in the presence of daylight or in the dark and thus is not subject to photo-initiation. At the end of the reaction, **(1)** is largely recovered unchanged with only a small amount of $[FeCl(CO)_2(\eta\text{-}cp)]$ being formed. In the absence of alkene, **(1)** reacts rapidly with $CCl_4$ to give the chloro-complex in quantitative yield.

$$\text{Rate} = \frac{k[\mathbf{1}][CCl_4][RCH{=}CH_2]}{k' + k''[RCH{=}CH_2]} \qquad (2)$$

A kinetic study of the reaction between $CCl_4$ and oct-1-ene in the presence of **(1)** at 40 °C shows the reaction to obey the



**Scheme 1**

rate law given in equation (2). The reaction rate is retarded when measured in the presence of CO (1 bar). The rate law is not consistent with a free radical chain mechanism in which **(1)** acts solely as an initiator or a mechanism in which cleavage of the dinuclear complex **(1)** into an active mononuclear catalyst is a rate determining step. Neither is a simple redox-catalysed process such as that observed in the presence of $[Mo_2(CO)_6(\eta\text{-}cp)_2]$ indicated.[1]

The reaction between oct-1-ene and a mixture of $CCl_4$ and $CBr_4$ in the presence of **(1)** at 40 °C gave only tetrachloro- and tetrabromo-nonane, no cross-over products ($C_6H_{13}CHClCH_2CBr_3$ and $C_6H_{13}CHBrCH_2CCl_3$) being formed. Such behaviour is inconsistent with a radical mechanism of the type displayed by $[RuCl_2(PPh_3)_3]$[2] and indicates a mechanism such as that shown in Scheme 1 or one in which tight radical pairs, such as **(2)**, are formed.† Reactions involving a $CCl_4$–$CBr_4$ mixture performed at higher temperatures (>80 °C) show considerable cross-over, suggesting that an alternative free radical mechanism obtains under these conditions.

In an attempt to differentiate between the mechanism shown in Scheme 1 and one involving tight radical pairs, we carried out the reaction of an alkene with $H_2$ in the presence of **(1)**. We reasoned that a mechanism such as that shown in Scheme 1 would be equally applicable to other addends, such as $H_2$, in place of $CCl_4$, whereas hydrogenation of a simple alkene would not be expected to proceed by a free radical route under mild conditions.[6] Reaction with cyclohexene proceeded slowly at 1 bar and 25 °C; however at 6 bar and 17 °C, a turnover to cyclohexane of 16 $h^{-1}$ was observed. When $[Fe_2(CO)_4(\eta\text{-}C_5Me_5)_2]$ **(3)** was employed in an analogous reaction, the turnover was 20 $h^{-1}$.

We suggest that the active catalyst in the reaction scheme is $[Fe_2(CO)_3(\eta\text{-}cp)_2]$ **(4)**, since the reaction is retarded by CO. This species has been shown to be formed when **(1)** is subjected to irradiation[7] and the analogue, $[Fe_2(CO)_3(\eta\text{-}C_5Me_5)_2]$ **(5)**, has been isolated and characterised.[8] It is

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† The di-iron radical of **(2)** may be viewed as being analogous to the paramagnetic species, $[Co_2(CO)_6\{\mu\text{-}P(CH_2SiMe_3)_2\}]$.[5]

pertinent that (**5**) has been shown to have a triplet ground state and may perhaps be viewed as a diradical. An alternative active species that does not require CO dissociation is (**6**), the singly bridged isomer of (**1**). The formation of (**6**) has been proposed in substitution reactions of (**1**);[9] however, independent studies have not confirmed its existence.[10,11] A mechanism similar to that shown in Scheme 1, but involving (**6**), would require an $\eta^5$ to $\eta^3$ ring slip during the catalytic cycle if an 18-electron configuration is not to be exceeded. Although we favour the mechanism shown in Scheme 1, we cannot definitively exclude a reaction proceeding *via* formation of (**6**), and presumably this intermediate would react with CO at the 16-electron metal centre, thereby retarding the rate.

The above data for the addition of either $CCl_4$ or $H_2$ to alkenes do not exclude mechanisms involving active mononuclear intermediates which recombine at the end of each cycle. To elucidate this point we performed reactions in the presence of a mixture of (**1**) and (**3**).‡ At 40 °C in the dark, $CCl_4$ addition to oct-1-ene proceeds at rate similar to those given in Table 1. Both (**1**) and (**3**) were recovered from the reaction mixture, but there was no evidence for the cross-over product, $[Fe_2(CO)_4(\eta\text{-cp})(\eta\text{-}C_5Me_5)]$ (mass spectrometry and i.r. spectroscopy). An analogous hydrogenation reaction also showed no evidence of metal cross-over. A similar approach has been used by Slater and Muetterties in their study of the hydrogenation of alkynes in the presence of $[Mo_2(CO)_4(\eta\text{-cp})_2]$.[12]

$[Ru_2(CO)_4(\eta\text{-cp})_2]$ (**7**) also promotes the reaction between $CCl_4$ and oct-1-ene, although its activity is less than that of the iron analogue. However, to our surprise, reactions of a $CCl_4$–$CBr_4$ mixture produced cross-over products at 40 °C. We ascribe this to the fact that (**7**) exhibits a much higher propensity than (**1**) to exist in the non-bridged form at elevated temperatures[13] and is thus much less likely to form intermediates such as (**4**). Thus (**7**) would be expected to show reactivity paralleling $[Mo_2(CO)_6(\eta\text{-cp})_2]$, which we have shown to catalyse such reactions by a mechanism involving free radicals.[2] We are engaged in a detailed study of reactions in the presence of (**7**).

The mechanism outlined in Scheme 1 is thus consistent with our findings. However, we are not able to exclude formation and reaction of an intermediate such as (**8**) and a similar scheme proceeding *via* (**8**) can be envisaged. In this context, it is noteworthy that $[Au(CH_2)_2PPh_2]_2$ has recently been reported to react with $CCl_4$ to give $[ClAu\{\mu\text{-}(CH_2)_2PPh_2\}_2AuCCl_3]$.[14] However, Randolph has shown (**4**) to react with $H_2$ to yield a species whose i.r. and $^1H$ n.m.r. spectra are consistent with the structure (**9**) in which oxidative addition has occurred at one metal centre.[15]

A mechanism similar to that shown in Scheme 1 is entirely consistent with the findings of Coville *et al.* in their study of the catalysis of ligand substitution in complexes of the type $[MX(CO)_nL_m]$ by (**1**).[16] Such a mechanism can also account for the ability of (**1**) to catalyse the isomerisation of 1,4-dichlorobut-2-ene;[17] however, as this reaction was performed at 90 or 120 °C, a radical mechanism cannot be excluded.

The title reactions thus join the small group of reactions shown to be catalysed by di- or poly-nuclear complexes[12,18] and they illustrate the way in which adjoining metal atoms and bridge–terminal ligand exchange can alter the electronic configuration of metal centres, thus promoting catalysis.

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‡ In independent reactions of $CCl_4$ and oct-1-ene we observed approximately equal rates in the presence of either (**1**) or (**3**) (see Table 1). Similar results were obtained for independent reactions of $H_2$ and cyclohexene in the presence of either (**1**) or (**3**) (see text). This allows us to conclude that it is unlikely that reactions in the presence of a mixture of (**1**) and (**3**) proceed by employing only one of them as a catalyst. No cross-over would be observed if this were the case.

Furthermore, cross-over between (**1**) and (**2**) would not be observed if neither were the active catalyst, but if catalysis occurred by virtue of the presence of a small amount of finely divided iron arising from decomposition of the complexes. In an independent reaction, we have found that metallic iron does indeed catalyse addition of halogenocarbons to alkenes; however, a reaction involving oct-1-ene and a $CCl_4$–$CBr_4$ mixture in the presence of this catalyst yields both homo-halogeno- and cross-over products (indicative of a free radical reaction). This is contrary to our observations involving catalysis by (**1**) in such reactions cited above. Furthermore we would not expect well behaved kinetics if catalysis depended on decomposition of (**1**).

## References

1 R. Davis and I. F. Groves, *J. Chem. Soc., Dalton Trans.*, 1982, 2281.

2 W. J. Bland, R. Davis, and J. L. A. Durrant, *J. Organomet. Chem.*, 1985, **280**, 397.

3 W. J. Bland, R. Davis, and J. L. A. Durrant, *J. Organomet. Chem.*, 1985, **280**, 95.

4 T. Susuki and J. Tsuji, *J. Org. Chem.*, 1970, **35**, 2982.

5 A. H. Cowley, R. A. Kemp, and J. C. Wilburn, *J. Am. Chem. Soc.*, 1982, **104**, 331.

6 J. F. Garst, T. M. Bockman, and R. Batlaw, *J. Am. Chem. Soc.*, 1986, **108**, 1689; F. Ungvary and L. Marko, *J. Organomet. Chem.*, 1981, **219**, 397; F. Ungvary, *Acta Chim. Hung.*, 1982, **111**, 117.

7 B. D. Moore, M. B. Simpson, M. Poliakoff, and J. J. Turner, *J. Chem. Soc., Chem. Commun.*, 1984, 972.

8 J. P. Blaha, B. E. Bursten, J. C. Dewan, R. B. Frankel, C. L. Randolph, B. A. Wilson, and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 4561.

9 D. R. Tyler, M. A. Schmidt, and H. B. Gray, *J. Am. Chem. Soc.*, 1983, **105**, 6018.

10 T. J. Meyer and J. V. Casper, *Chem. Rev.*, 1985, **85**, 187, and references therein.

11 M. Poliakoff, personal communication.

12 S. Slater and E. L. Muetterties, *Inorg. Chem.*, 1980, **19**, 3337.

13 M. A. Bennett, M. I. Bruce, and T. W. Matheson, 'Comprehensive Organometallic Chemistry,' vol. 4, ch. 32.4, eds. G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford, 1982, and references therein.

14 H. H. Murray, J. P. Fackler, L. C. Porter, and A. M. Mazany, *J. Chem. Soc., Chem. Commun.*, 1986, 321.

15 C. L. Randolph, Ph.D. Thesis, Massachusetts Institute of Technology, 1985.

16 N. J. Coville, M. O. Albers, and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1983, 947.

17 G. Henrici-Olivé and S. Olivé, *J. Organomet. Chem.*, 1971, **29**, 307.

18 R. D. Adams and I. T. Horvarth, *Prog. Inorg. Chem.*, 1985, **33**, 127; E. L. Muetterties and M. J. Krause, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 135.